

## UNPUBLISHED THE HALLAMY DATA

X-Ray and Infrared Studies of Several Ruthenium-Sulfur Dioxide Complexes

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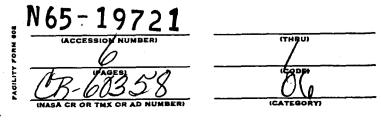
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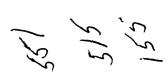
The infrared and x-ray powder data for several Ru-SO<sub>2</sub> complexes is interpreted on the basis of the results for the crystal and molecular structure study of the  $\{Ru^{II}(NH_3)_4(SO_2)CI\}CI$  complexe. Three complexes

(2) L. H. Vogt, Jr., J. L. Katz, and S. E. Wiberley, <u>Inorg</u>. <u>Chem.</u>, \_\_\_, (1965).

were investigated, viz.,  $[Ru^{II}(NH_3)_4(SO_2)Br]Br$ ,  $[Ru^{II}(NH_3)_5(SO_2)]Cl_2$ , and  $[Ru^{II}(NH_3)_5(SO_2)]Br_2$ . The bromo-bromide was prepared in a manner exactly analogous to the chloro-chloride complex by substituting HBr for HCl in the conversion of  $[Ru^{II}(NH_3)_4(HSO_3)_2]$  to the  $SO_2$  complex. The dichloride and dibromide can be obtained from either the chloro-chloride or bromo-bromide complexes by the method described in the literature. Both the

(3) K. Gleu and W. Breuel, Z. anorg. u. allgem. Chem. 235. 211 (1938).





dichloride and dibromide complexes decomposed after standing at room temperature for about 1-2 months.

Examination of the x-ray powder pattern and preliminary single crystal precession photographs of  $[Ru^{II}(NH_3)_4(SO_2)Br]Br$  shows that this complex has an orthorhombic unit cell with a=14.35, b=9.51, c=7.45 Å ± 0.2% (estimated). The density, measured by floatation, is  $2.45 \pm 0.05$  g./cc. at 24° (corresponding to four formula weights per unit cell). Space group absences for Okl,  $k+l\neq 2n$ ; hkO,  $h\neq 2n$ ; hOO,  $h\neq 2n$ ; OkO,  $k\neq 2n$ ;  $OOl\neq 2n$ , are consistent with either  $Pna2_1$  or Pnam. Thus, the bromo-bromide and chloro-chloride complexes appear to be isomorphous. Three-dimensional data for the bromo-bromide complex presently are being collected by counter methods similar to those used for the chloro-chloride<sup>2</sup>, with the intent of obtaining a detailed structure analysis.

Comparison of the powder patterns of the complexes (Table I) afforded a qualitative method of determing whether or not their crystal structures were isomorphous. The pattern of the bromo-bromide was consistent with the conclusions drawn from the single crystal data. In the case of the dichloride complex, however, departure from the chloro-chloride pattern was evidenced by splitting of some of the corresponding medium intensity lines in the former, into doublets, suggesting deviation from orthorhombic to lower symmetry. The pattern for the dibromide complex was dissimilar to the patterns of the other complexes. It is anticipated that three-dimensional crystal structure analyses of the dichloride and dibromide complexes will be undertaken in the near future.



The infrared spectra of the complexes showed bands characteristic of the  $NH_3$  ligand (Table II) as well as the four bands (Table III) attributed to the  $SO_2$  ligand in  $[Ru^{II}(NH_3)_4(SO_2)C1]C1.^2$ 

Thus, it is concluded that the crystal and molecular structure of the bromo-bromide and chloro-chloride complexes are, on the basis of the x-ray and infrared data, completely analogous. The dichloride and dibromide complexes have crystal structures which differ both one from the other and from that of the chloro-chloride complex. However, the similarity of the infrared spectra of the former two complexes to the latter indicates that the SO<sub>2</sub> ligand is coordinated in the same way in all of the complexes, i.e., through the sulfur.

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(Cont.)

Table I

		Te I		
Observed Interpl	anar Spacings <sup>a</sup>	(in Å) for Sev	eral Ru-SO, Co	mplexes
$^{ m II}_{ m (NH_3)_{4}(S\Theta_2)C1]C1}$	م <sub>ل</sub>	. م	<del>vo</del> 2	
Ę	[Ru <sup>II</sup> (NH3)4(SO <sub>2</sub> )Br]Br <sup>b</sup>	$[ m _{Ru}^{II}( m _{NH_3})_5( m _{502})]{ m cl}_2^{ m \ b}$	ບໍ່	
0	Br	<u> </u>	ř.	
9	2)	. (2		
S <sub>2</sub>	SO	SS S	75)	
7	<b>)</b>	5	(8	
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, E	ົສ	<u>ያ</u>	11	
	<b>=</b>	_	$[Ru^{ ext{II}}(NH_3)_5(SO_2)]Br_2^{ ext{c,d}}$	
5.713 s	5.821 w	5.897 s	6.45 w	
5.589 s	5.673 s	5.745 s	6.15 s	
5.019 m	5.169 w	5.101 w	5.85 w	
4.405 vw	4.244 s	5.016 w	5.65 s	
4.156 w	3.844 vw	4.341 vw	4.52 m	
3.857 vw	3.755 m	4.174 vw	4.15 w	
3.768 vw	3.489 w	3.963 w	4.05 m	
3.643 ms 3.406 m	3.136 w	3.697 vw	3.60 s	
3.270 vw	3.071 vw	3.624 w	3.51 s	
3.142 vw	2.941 vw 2.908 vw	3.582 s	3.49 s	
3.047 m	2.887 vw	3.487 vw	3.39 vw	
2.846 w	2.819 m	3.365 vw 3.325 vw	3.23 m	
2.801 w	2.741 vw	3.125 vw	3.10 w	
2.740 m	2.692 vw	3.071 m	3.05 vw 2.95 m	
2.640 w	2.631 w	3.009 w	2.85 m	
2.603 w	2.501 vw	2.819 vw	2.76 m	
2.575 w	2.369 m	2.794 vw	2.59 wm	
2.433 m	2.334 w	2.736 w	2.50 vw	
2.316 w	2.154 vw	2.715 vw	2.38 vw	
2.295 w	2.134 m	2.680 vw	2.32 vw	
2.207 wm	2.122 w	2.622 vw	2.06 m	
2.157 wm	2.058 vw	2.556 wm		
2.082 wm	2.049 vw	2.516 wm		
2.058 w 1.993 w	2.005 m	2.470 vw		
1.955 wm	1.986 vw	2.406 vw		
1.941 vw	1.969 vw 1.930 vw	2.355 wm		
1.913 vw	1.913 vw	2.314 w		
	1.913 VW	2.282 wm 2.260 vw		
		2.230 vw		
		2.211 vw		
		2.154 vw		,
		2.089 wm		
		2.064 vw		
		2.001 vw		
		1.989 vw		
		1.971 vw		
		1.957 vw		
		1.926 vw		
		1.907 ww		(Cont.)

- a. The patterns were recorded on film, using a Debye-Scherrer camera and CrKo radiation.
- b. Estimated to  $\pm$  0.005 Å.
- c. Estimated to  $\pm 0.01 \text{ Å}$ .
- d. Many extremely weak lines are not reported.

Table II

Infrared Frequencies (in	cm1) of	the NH <sub>3</sub> ligand	in Ruthenium	-Ammine-SO <sub>2</sub>	Complexes
Complex	Sym. Str.	Asy. Str.	Sym. Def.	Asy. Def.	Rock
$[Ru^{II}(NH_3)_4(SO_2)C1]C1$	3225(s)	3420(ms)	1245(s)	1625(m)	• 779 (m)
$[Ru^{II}(NH_3)_4(SO_2)Br]Br$	3225(s)	3420(s)	1248(s)	1618(m)	763(m)
$[Ru^{11}(NH_3)_5(SO_2)]C1_2$	3205(s)	3425(s)	1240(s)	1625(m)	808(m)
$[Ru^{II}(NH_3)_5(SO_2)]Br_2$	3215(s)	3410(ms)	1260(s)	1620(m)	805(m)

Complex	Sym. Str.	Asy. Str.	Bend
$[Ru^{\overline{1}\overline{1}}(NH_3)_4(SO_2)C1]C1$	1100(s)	1301 1278 (s)	552(m)
[Ru <sup>II</sup> (NH <sub>3</sub> ) <sub>4</sub> (SO <sub>2</sub> )Br]Br	1100(s)	1299 1278 (s)	550(m)
$[Ru^{II}(NH_3)_5(SO_2)]Cl_2$	1098(s)	1303 1255 (s)	548(m)
$[Ru^{II}(NH_3)_5(SO_2)]Br_2$	1117(s)	1327 1301 (s)	551(m)